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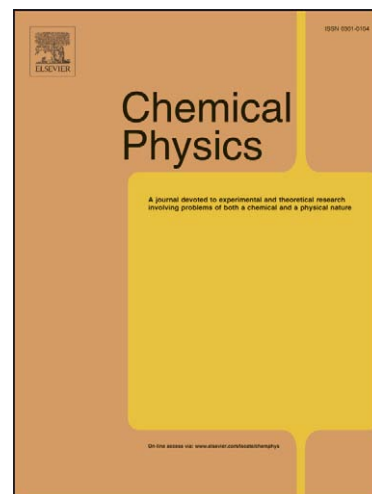
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Iodopentafluorobenzene: electronic state spectroscopy by high resolution vacuum ultraviolet photoabsorption and photoelectron spectroscopy

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Abstract

The electronic transitions of iodopentafluorobenzene (C_6F_5I) have been investigated experimentally for the first time by high-resolution photoabsorption spectroscopy in the energy range 3.6 – 10.7 eV. The character of the valence excited states has been discussed taking into account calculations available in the literature. The ionisation energies of the molecule in its electronic ground state have been measured by high-resolution He(I) photoelectron spectroscopy. The energies of the ionic bands are shifted by about 0.5 eV compared to the earliest literature values but they agree with the most recently published measurements. All the spectra presented in this paper represent highest resolution measurements of their kind for iodopentafluorobenzene. The absolute photoabsorption cross sections have been used to model photolysis rates and residence times in the terrestrial atmosphere.

Key words: lifetimes, photolysis, plasmas, VUV photoabsorption cross sections, photoelectron spectroscopy

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1. Introduction

Iodopentafluorobenzene (C_6F_5I) is a perfluorinated iodised compound which is principally used in the preparation of catalysts. The species also has potential applications in the plasma processing industry [1]. It is therefore timely to evaluate the effects of the emission of iodopentafluorobenzene into the terrestrial atmosphere. The present UV spectrum and absolute cross sections provide a reference to monitor the concentration of C_6F_5I in the atmosphere as well as in industrial gases or plasmas. Moreover this data can be used to predict the effects of solar UV radiation on the molecule, notably in terms of fragmentation pathways and photolysis rates. In perfluorinated molecules such as hexafluorobenzene (C_6F_6), the C-F bonds are much stronger than equivalent C-I bonds [2]. Accordingly C_6F_5I is expected to be photolysed efficiently with the release of highly-reactive iodine atoms. Iodine produced by solar UV radiation in the stratosphere can accelerate ozone depletion through catalytic reactions. In addition, gas-phase C_6F_5I is known to react with Br_2 to produce the highly reactive species Brl [3], a very efficient destroyer of stratospheric ozone. Furthermore, the formation of CF_x^{\bullet} radicals and ions needed in semiconductor plasma reactors for silicon etching is dependent on the dissociation dynamics of the neutral excited and ionic states.

Despite the considerable interest in the physical and chemical properties of C_6F_5I and in the production of reactive I and C_yF_x fragments, there is little spectroscopic data in the literature on the excited states of the neutral molecule and the positive ion. To the authors' knowledge, only one UV photoabsorption spectrum has been reported [4] in the range 330 - 205 nm (3.8 - 6.0 eV) as part of a paper focusing on photo-dissociation dynamics. This work discusses assignments for transitions in the lowest-energy valence bands but does not provide absolute photoabsorption cross sections. No electron impact experiments have been carried out to probe the valence and Rydberg states of iodopentafluorobenzene. *Ab initio* calculations for the photo-dissociation and vertical excitations of the neutral excited states have been reported by Ajitha et al. [5], taking into account the spin-orbit splitting of iodine [5]. Comparisons with the calculated results for the non-fluorinated molecule iodobenzene (C_6H_5I) led the authors to discuss the effect of perfluorination on photo-dissociation and valence excitation energies. The only two photoelectron spectra available in the literature [6, 7] are not in good agreement with each other: a systematic shift of ~ 0.5 eV differentiates the data sets. The first study [6] was performed with the same energy resolution as the present work but the authors did not explain

how they have calibrated the energy scale. The more recent spectrum [7] was calibrated using argon but was carried out at lower resolution than the present measurement, revealing less detailed structure.

The present study provides new reference data to characterise the electronic excited states of $\text{C}_6\text{F}_5\text{I}$ for both the neutral molecule and the positive ion using high-resolution VUV photoabsorption and He(I) photoelectron spectroscopies. In addition, the photolysis rate of this industrial molecule in the terrestrial atmosphere has been modelled for the first time.

2. Experimental

The electronic states of iodopentafluorobenzene have been studied using two complementary techniques. Firstly, VUV spectroscopy measurements with a synchrotron radiation source provided data on optically allowed transitions and absolute photoabsorption cross sections. Secondly, He(I) photoelectron spectroscopy (PES) experiments determined the ionisation energies of the outermost molecular orbitals occupied in the neutral electronic ground state.

2.1. VUV photoabsorption

The high-resolution VUV photoabsorption measurements were performed using the ASTRID – UV1 beam line at the Institute for Storage Ring Facilities (ISA), University of Aarhus, Denmark. A detailed description of the apparatus can be found elsewhere [8]. Briefly, a toroidal dispersion grating is used to select the synchrotron radiation with a Full Width at Half Maximum (FWHM) wavelength resolution of approximately 0.075 nm (corresponding to 3 meV at the midpoint of the energy range studied). The synchrotron radiation passes through the static gas sample at room temperature and a photo-multiplier is used to detect the transmitted light. For wavelengths below 200 nm (energies above 6.20 eV), He gas is flushed through the small gap between the photomultiplier and the exit window of the gas cell to prevent any absorption by air contributing to the spectrum. The LiF entrance window acts as an edge filter for higher order radiation, restricting the photoabsorption measurements to wavelengths above 115.5 nm (energies below 10.73 eV). The grating itself determines 350.0 nm as the maximum wavelength which can be studied at the ASTRID UV-1 beam line (low energy limit of 3.54 eV). The sample pressure is measured using a Baratron capacitance gauge. To avoid any saturation effects, sample pressures were chosen such that the transmitted flux was > 10% of the incident flux.

Gas transmission results are compared to a background scan recorded with an evacuated cell. Absolute cross sections may then be calculated using the Beer-Lambert law:

$$I_t = I_0 \exp(-n\sigma x)$$

where I_t is the intensity of the light transmitted through the gas sample, I_0 is that through the evacuated cell, n is the molecular number density of the sample gas, σ is the absolute photoabsorption cross section and x is the absorption path length (25 cm). The uncertainty on the absolute cross section measurements is estimated at $\pm 5\%$ [8]. Only when absorption by the sample is very weak ($I_0 \approx I_t$), does the uncertainty increase as a percentage of the measured cross section.

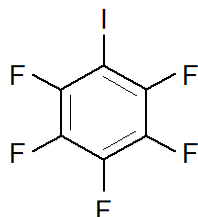
2.2. Photoelectron spectroscopy (PES)

The He(I) (21.22eV) photoelectron spectrum of iodopentafluorobenzene was measured at the Université de Liège, Belgium. The apparatus has been described in detail previously [9]. Briefly, it consists of a 180° hemispherical electrostatic analyser with a mean radius of 5 cm. The analyser is used in the constant pass energy mode. The incident photons are produced by a D.C. discharge in a two-stage differentially pumped lamp. The energy scale is calibrated using the $X^2\Sigma_g^+$, $v' = 0$ [10] and $A^2\Pi_u$, $v' = 0$ [11] peaks of N_2^+ , rounded to three decimals. The resolution of the present spectrum is 20 meV and the accuracy of the energy scale is estimated to be ± 2 meV. In addition, the two first bands of the spectrum have been deconvoluted using the procedure described by van Cittert [12] and subsequently modified by Allen and Grimm [13]. The intensities in the spectrum were corrected for the transmission of the analyzing system. The photoelectron spectrum presented in this paper is the sum of 135 individual spectra. This procedure allows us obtain a good signal-to-noise ratio while keeping the pressure in the spectrometer low ($< 5 \times 10^{-6}$ mbar), thus minimizing the occurrence of dimers.

2.3. Iodopentafluorobenzene sample

The sample was provided by Sigma Aldrich with a stated purity better than 99%. It was used directly without further purification except for repetitive freeze-pump-thaw cycles in order to eliminate air and other volatile substances present in the sample.

3. Properties of Iodopentafluorobenzene



In the gas phase, the molecule belongs to the C_{2v} symmetry class in its electronic ground state, in contrast with hexafluorobenzene which belongs to the D_{6h} symmetry group. The electronic structure for the external occupied and unoccupied molecular orbitals is [5] :

$$\dots\dots (n^{\parallel}-\pi)b_2^2 (\sigma)a_1^2 (\pi)b_2^2 (n^{\perp})b_1^2 (\pi)a_2^2 (n^{\parallel}-\pi)b_2^2 \\ (\sigma^*)a_1^0 (\pi^*)a_2^0 (\pi^*)b_2^0 (\pi^*)b_2^0$$

The molecule has 30 normal vibration modes with twenty fundamental vibrations [14].

The normal vibration modes identified by Hyams et al. [14] are summarised in Table 1. Comparisons with hexafluorobenzene (D_{6h}) [9] and bromopentafluorobenzene (C_{2v}) [15] helped in the assignments.

4. Results and Discussion

4.1. Valence and Rydberg states

The high resolution absolute VUV photoabsorption spectrum has been recorded between 3.6 and 10.7 eV and is shown in Figure 1. It consists of two regions, the first comprising broad bands between 3.6 and 8.0 eV and the second rather sharp bands with fine structure from 8.0 to 10.7 eV. The absorption cross section in the Rydberg state region is far greater than in hexafluorobenzene [9] and in bromopentafluorobenzene [15]. In compounds containing heavy atoms such as bromine or iodine, spin forbidden transitions might be excited with non negligible intensity [16]. The present tentative assignments for the valence excited neutral states stem principally from comparisons with the available *ab initio* calculations in the literature [5].

4.1.1. Valence transitions

The energies of the experimental bands observed in this region are given in Table 2. Figure 1 shows that all except the last band (F centred at 7.933 eV) are quite broad, suggesting rapid dissociation of the excited states into neutral radicals. The energy positions of the lowest energy bands are generally in good agreement with the only previous spectrum (3.8 - 6.0 eV) [4], although Kavita et al.'s measurement suggests different structure in the C band than apparent in the present work. We suspect that these differences may be attributable to noise in the previous spectrum [4]. Bands A-C are shifted to slightly lower energies in the present work

compared to the corresponding transitions in hexafluorobenzene [9] whereas bands D and E are located at slightly higher energies. The calculations [5] predicted only $n\text{-}\sigma^*$ and $\pi\text{-}\pi^*$ type transitions (no $n\text{-}\pi^*$ type). The authors calculated energies of 4.30 eV for the $n\text{-}\sigma^*$ transition to the triplet state (band A) and of 4.88 eV for the corresponding singlet (located in band B). For the $\pi\text{-}\pi^*$ transitions to the 3B_1 and 1B_1 electronic excited states, the calculated energies are 4.86 eV and 5.05 eV, respectively. The triplet state excitations (spin forbidden transitions) in the A and B bands are considered to be too weak to be clearly resolved from the $n\text{-}\sigma^*$ singlet transition at 4.736 eV. Indeed the low absolute cross sections of all three observed transitions in the A and B bands are consistent with symmetry-forbidden excitations. The C band, measured at 5.585 eV may correspond to the $\pi\text{-}\pi^*$ transition to the 1B_1 state.

Assignments in bands D-F are complicated by the overlap of valence and Rydberg states (see section 4.1.2). The large absolute cross section of the E band at 7.354 eV (maximum of 110 Mb at 7.354 eV) is evidently due to an optically allowed transition. The corresponding band located at 7.10 eV in hexafluorobenzene [9] has been assigned to the $\pi\text{-}\pi^*$ ($X^1A_{1g}\text{-}1^1E_{1u}$) excitation (Table 2). In addition to these broad features, the band centred at 7.93 eV (band F) exhibits seven fine features regularly spaced by 26 meV. This suggests excitation of a valence state which is at least partially stable with respect to dissociation. Comparison with the energies of vibrational modes in the neutral ground state (Table 1) suggests that this vibrational structure may be attributed to the normal modes, ν_{11} , ν_{29} (both in the plane of the benzene-type ring), and / or ν_{18} (perpendicular to the plane of the ring).

4.1.2. Rydberg transitions

The photoabsorption spectrum in the 8.0-10.7 eV region is shown in detail in Figure 2. It is characterised by series of typically quite sharp features converging to the four lowest energy ionisation limits at 9.405, 9.844 eV, 10.479 eV, and 11.213 eV (see section 4.2). Transitions have been assigned, tentatively, using the Rydberg formula: $E_n = E_i - R/(n-\delta)^2$, where E_n is the peak energy, E_i the ionisation energy, n the principal quantum number of the Rydberg orbital, R the Rydberg constant, and δ the quantum defect due to the penetration of the Rydberg orbital into the core. Quantum defects for iodised compounds typically range from 3.9 to 4.2 for ns series, 3.3 to 3.7 for np series, and 2.0 to 2.5 for nd series.

Table 3 presents the Rydberg series converging to the ground ionic state (9.405 eV) and to the first ionic excited state (9.844 eV). The first member of the *ns* series converging to 9.405 eV is observed at 6.36 eV as a shoulder on the low-energy side of the valence band centred at 6.968 eV. Four further terms have been assigned to this *ns* series with quantum defects around 3.9. For the *np* series converging to 9.405 eV, seven terms have been identified with quantum defects around 3.5 (Table 3). The $n=6$ term at 7.23 eV manifests itself as a shoulder on the low-energy side of the intense valence band centred at 7.354 eV (Figure 1). Only four members for the *nd* series converging to the ground ionic state have been assigned, each with a quantum defect around 2.2.

The $n=6$ origin of the *ns* series converging to the first excited ionic state appears as a shoulder at 6.85 eV on the high-energy side of the valence D band (Figure 1). Three further terms have been assigned to this series with quantum defects around 3.9 (Table 3). The three transitions assigned to the *np* series converging to 9.844 eV have quantum defects around 3.2. For the *nd* series converging to 9.844 eV, six terms ($n=5-10$) have been identified with quantum defects around 2.4.

The Rydberg series converging to the two higher ionisation limits at 10.479 eV and 11.213 eV are summarised in Table 4. The $n=6$ term of the *ns* series converging to 10.479 eV manifests itself as a weak shoulder at 7.09 eV on the low-energy side of the valence band E (Figure 1). Five further features have been assigned to this *ns* series with quantum defect values around 4.0 (Table 4). Also converging to 10.479 eV, five transitions have been assigned to an *np* series and five to an *nd* series (quantum defects around 3.5 and 2.0, respectively).

Only two Rydberg series have been identified converging to the ionisation limit at 11.213 eV (Table 4). A first series with quantum defect values around 4.05 suggests an *ns* series. The first term is observed at 7.768 eV. A second series with four members corresponds to quantum defects around 2.5, consistent with an *nd* character.

4.2. Ionic states

Figure 3 shows the He(I) photoelectron spectrum of iodopentafluorobenzene recorded between 9.0 eV and 16.6 eV. The band structure is broadly consistent with the He(I) spectrum reported by Boschi and Salahub [6] but more fine features are resolved in the present work. Moreover

the energies of all the bands in the present data are approximately 0.5 eV lower than in Boschi and Salahub's spectrum [6]. The present energies of A1 (9.405 eV) and A2 (9.574 eV) (Table 5, Figures 3 and 4) agree very well with Trudell and Price's vertical value of 9.54 eV [7], corresponding to the mean of A1 and A2 in our study. The good agreement of the present spectrum with the previous work [7] is maintained at higher energies (e.g. E2 and F1 in Table 5).

Only the bands A-G (Figure 3) associated with the lowest energy ionic states are discussed in the present study. With the exception of F1, fine structure is observed in all the bands (summarised in Table 5). To the authors' knowledge, no *ab initio* calculations have been carried out for the ionic states of iodopentafluorobenzene; the only theoretical study available in the literature is based on semi-empirical calculations using a modified CNDO method [6]. Following these CNDO calculations, the bands have been assigned to ionisation from the two lowest-energy π type orbitals of the molecule in its neutral electronic ground state. The first ionic band (Figure 3) starts at 9.405 eV (Table 5). The following feature, 169 meV higher, is attributed to vibrational excitation of the ground ionic level. Comparison with the neutral electronic ground state vibrational energies (Table 1) suggests that this feature may be due to excitation of the ν_3 mode (174 meV), ν_4 (160 meV), ν_{22} (188 meV), and/or ν_{23} (157 meV) modes.

For the second ionisation limit at 9.844 eV the spectral band shows two series with a mean spacing of 190 meV and 80 meV, respectively. Comparisons with vibrational energies in the neutral ground state (Table 1) suggests that this structure may include contributions from the ν_7 , ν_{15} , or ν_{26} , and ν_2 / ν_{22} modes. The rather sharp shape of the next band at 10.479 eV (Figure 3) suggests ionisation from the iodine lone pair to an out-of-plane excited ionic orbital in agreement with Boschi and Salahub [6]. Four fine features with a mean spacing of 100 meV are tentatively assigned to vibrational excitation of ν_6 by comparison with its vibrational energy in the neutral ground state (Table 1).

The relatively diffuse band beginning at 11.213 eV has been assigned to a π type excited ionic state involving the iodine n lone pair [6] and corresponds to the in-plane orbital. Five fine features in this band can be attributed to two series of vibrational levels. The first series with a mean spacing of 189 meV may be assigned to the excitation of the ν_2 and/or ν_{22} modes; the second series with a mean spacing of 89 meV may be due to excitation of ν_{26} (see Table 1).

The bands beginning at 10.479 eV and at 11.213 eV are separated by 0.734 eV, close to the energy separation of the corresponding bands in iodobenzene [17]. This confirms the assignment to the iodine atom lone pair molecular orbitals. They are shifted to higher energies compared to iodobenzene [17] due to the presence of fluorine atoms [18].

The E band beginning at 12.678 eV exhibits only three partially-resolved fine features (Figure 3) separated by 180 meV and 198 meV (Table 5). Comparison with the vibrational energies in the neutral ground state (Table 1) suggests that this structure may be assigned to the normal vibration modes ν_2 and/or ν_{22} , and ν_1 and/or ν_{21} , respectively.

5. UV Photolysis rates

To the author's knowledge the present work provides the first absolute photoabsorption cross section values in the VUV energy range. Combined with solar actinic flux [19] measurements from the literature, these cross sections have enabled atmospheric UV photolysis rates of C_6F_5I to be calculated as a function of altitude from the Earth's surface to the stratopause at 50 km. The quantum yield for dissociation by the solar radiation is assumed to be unity and the reciprocal of the photolysis rate at a given altitude corresponds to the local photolysis *lifetime*, i.e. the time taken for the molecule to photo-dissociate assuming that the solar flux remains constant.

Figure 5 shows that the calculated photolysis lifetimes are very short for all altitudes (~ 1 sunlit hour at 0 km; < 5 sunlit minutes at 50 km). This indicates that C_6F_5I can be broken up very efficiently by UV photolysis in the lower atmosphere, releasing reactive iodine atoms through different dissociative channels as shown by Kavita and Das [4] and Ajitha et al. [5]. Therefore, emissions of the species close to the Earth's surface will not affect chemical processes at higher altitudes as the molecule's photolysis lifetime is very short compared to typical atmospheric transport times. Below 20 km, the local lifetime will also be determined by competing pathways for removal from the atmosphere i.e. solubility in water droplets and reactions with OH^\bullet radicals. The photolysis lifetimes of iodopentafluorobenzene in the lower atmosphere are much shorter than those of hexafluorobenzene [9] and bromopentafluorobenzene [15].

Conclusions

The full range of neutral valence and Rydberg excited states of C_6F_5I have been studied by high-resolution UV photoabsorption for the first time. In addition, high-resolution He(I) photoelectron spectroscopy measurements have revealed new structure in the ionic excited states of iodoperfluorobenzene. Most of the valence bands are quite broad, suggesting rapid dissociation or pre-dissociation of the electronically excited neutral molecule. Only one valence band (labelled F and centred at 7.933 eV) exhibits fine structure, typical of a transition to a relatively stable excited state accompanied by vibrational excitation. The ionisation energies agree quite well with the most recent values [7]. The photolysis of iodoperfluorobenzene in the lower atmosphere (altitudes below 50 km) has been modelled for the first time using the present absolute photoabsorption cross sections. The very short calculated lifetimes (~ 1 hour or less) indicate that C_6F_5I emissions at the Earth's surface will not have significant effects on stratospheric processes such as ozone depletion.

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Table 1: Symmetries, description, energies, and wavenumbers of the normal vibrational modes of iodopentafluorobenzene in the neutral electronic ground state (from reference 14)

Symmetry	Normal mode*	Energy (meV)	Wavenumbers (cm ⁻¹)
a ₁	v ₁	202	1633
	v ₂	187	1507
	v ₃	174	1406
	v ₄	161	1296
	v ₅	134	1083
	v ₆	100	805
	v ₇	72	581
	v ₈	61	489
	v ₉	43	349
	v ₁₀	34	278
	v ₁₁	25	204
a ₂	v ₁₂	?	?
	v ₁₃	47	381
	v ₁₄	14	110
b ₁	v ₁₅	74	600
	v ₁₆	?	?
	v ₁₇	43	349
	v ₁₈	27	217
	v ₁₈	16	133
	v ₂₀	14	114
b ₂	v ₂₁	202	1633
	v ₂₂	188	1517
	v ₂₃	157	1263
	v ₂₄	142	1149
	v ₂₅	125	1005
	v'	121	977
	v ₂₆	89	714
	v ₂₇	54	438
	v ₂₈	39	311
	v ₂₉	27	215
	v ₃₀	16	129

* Labelled following Hyams et al.'s [14] summary of the vibrational modes of C₆F₆. The mode labelled v' in the present work as only listed for C₆F₅X (X = Cl, Br, I) by Hyams et al. [14].

Table 2: Energies (eV) of the valence bands of iodopentafluorobenzene measured by photoabsorption and compared with *ab initio* calculations and analogous measurements for C₆F₆ and C₆F₅Br.

Bands	C ₆ F ₅ I (present work)	C ₆ F ₅ I calculations [5] ^a	C ₆ F ₅ Br [15]	C ₆ F ₆ [9]	Assignments for C ₆ F ₆ [9]
A	4.2	4.30 T n-σ*	4.785	4.86	π-π* 1 ¹ B _{2u}
B	4.736	4.86 T π-π*/4.88 S n-σ*	5.161	5.38	π-σ*
C	5.585	5.05 S π-π*	5.942	5.66	π-σ*
D	6.698	6.517	6.114	6.39	π-π* 1 ¹ B _{1u}
E	7.354	7.549	6.845	7.10	π-π* 1 ¹ E _{1u}
F	7.932				

^a S and T denote transitions to singlet and triplet states, respectively. In the present spectrum, the singlet transition centred at 4.736 eV obscures the triplet transitions in the A and B bands.

Table 3: Energies, quantum defects, and proposed assignments for Rydberg series converging to the two lowest ionisation limits of iodopentafluorobenzene (9.405 and 9.844 eV)

Limit at 9.405 eV			Limit at 9.844 eV		
Energy (eV)	Quantum defect	Assignment	Energy (eV)	Quantum defect	Assignment
6.36 ^b	3.89	6s	6.85 ^b	3.88	6s
8.061	3.82	7s	8.457	3.91	7s
8.622	3.83	8s	9.017 ^{*1}	4.04	8s
8.850	4.05	9s	9.308	4.14	9s
9.017 ^{*1}	4.08	10s	8.088	3.25	6p
7.23 ^b	3.50	6p	8.88 ^b	3.32	7p
8.266	3.54	7p	9.280	3.25	8p
8.812 ^{*2}	3.21	8p	7.857	2.41	5d
8.96 ^{b *3}	3.47	9p	8.812 ^{*2}	2.44	6d
9.10 ^b	3.32	10p	9.197	2.55	7d
9.18 ^b	3.22	11p	9.436	2.49	8d
9.24 ^b	2.92	12p	9.545 ^{*4}	2.66	9d
7.63 ^b	2.23	5d	9.626 ^{*5}	2.74	10d
8.44 ^b	2.25	6d			
8.812 ^{*2}	2.21	7d			
8.984	2.32	8d			

^b Indicates that the transition appears as a shoulder in the present spectrum and thus its energy is given to lower precision than that of a distinct peak

^{*} Indicates a feature which has alternative or overlapping suggested assignments

Table 4: Energies, quantum defects, and proposed assignments for Rydberg series converging to the two highest energy ionisation limits of iodopentafluorobenzene at 10.479 and 11.213 eV

Limit at 10.479 eV			Limit at 11.213 eV		
Energy (eV)	Quantum defect	Assignment	Energy (eV)	Quantum defect	Assignment
7.09 ^b	4.00	6s	7.77 ^b	4.01	6s
8.96 ^{b *3}	4.01	7s	9.626 ^{*5}	4.07	7s
9.545 ^{*4}	4.18	8s	10.367	3.99	8s
9.951	3.92	9s	10.642	4.12	9s
10.129 ^{*6}	3.77	10s	9.123	2.45	5d
8.30 ^b	3.50	6p	10.129 ^{*6}	2.46	6d
9.35 ^b	3.53	7p	10.561	2.43	7d
9.80 ^b	3.52	8p	10.707	2.81	8d
10.015	3.58	9p			
10.15 ^b	3.57	10p			
8.939	2.03	5d			
9.626 ^{*5}	2.01	6d			
9.93 ^b	2.02	7d			
10.129 ^{*6}	1.77	8d			
10.221	1.74	9d			

^b Indicates that the transition appears as a shoulder in the present spectrum and thus its energy is given to lower precision than that of a distinct peak

* Indicates a feature which has more than one suggested assignment

Table 5: Energies and assignments of the bands in the He(I) photoelectron spectrum of iodopentafluorobenzene

Band	Energy (eV)			Assignment (assuming C_6F_6 symmetry) [6]
	This work	Trudell and Price [7]	Boschi and Salahub [6]	
A1	9.405	9.54	9.84	$e_{1g}\pi$
A2	9.574			
A3	9.732			
B1	9.844		10.26	π
B2	9.916			
B3	10.036			
B4	10.126			
B5	10.226			
C1	10.479	10.5 ^c	10.96	n lone pair
C2	10.578			
C3	10.673			
C4	10.779			
D1	11.213	11.2 ^c	11.72	π lone pair
D2	11.303			
D3	11.401			
D4	11.489			
D5	11.591			
E1	12.678	12.85	13.2	$1a_{2u}\pi$
E2	12.858			
E3	13.056			
F1	13.413	13.48	13.9	$2e_{2g}\sigma$
G1	13.854			
G2	14.022			
G3	14.207			
G4	14.397			
H1	14.790			
H2	14.936			
J1	15.298			

^c Value estimated from a figure in Trudell and Price's publication [7]

Figure 1: The absolute absorption cross section (Mbarn = 10^{-18} cm²) of iodopentafluorobenzene in the range 3.6 -10.7 eV

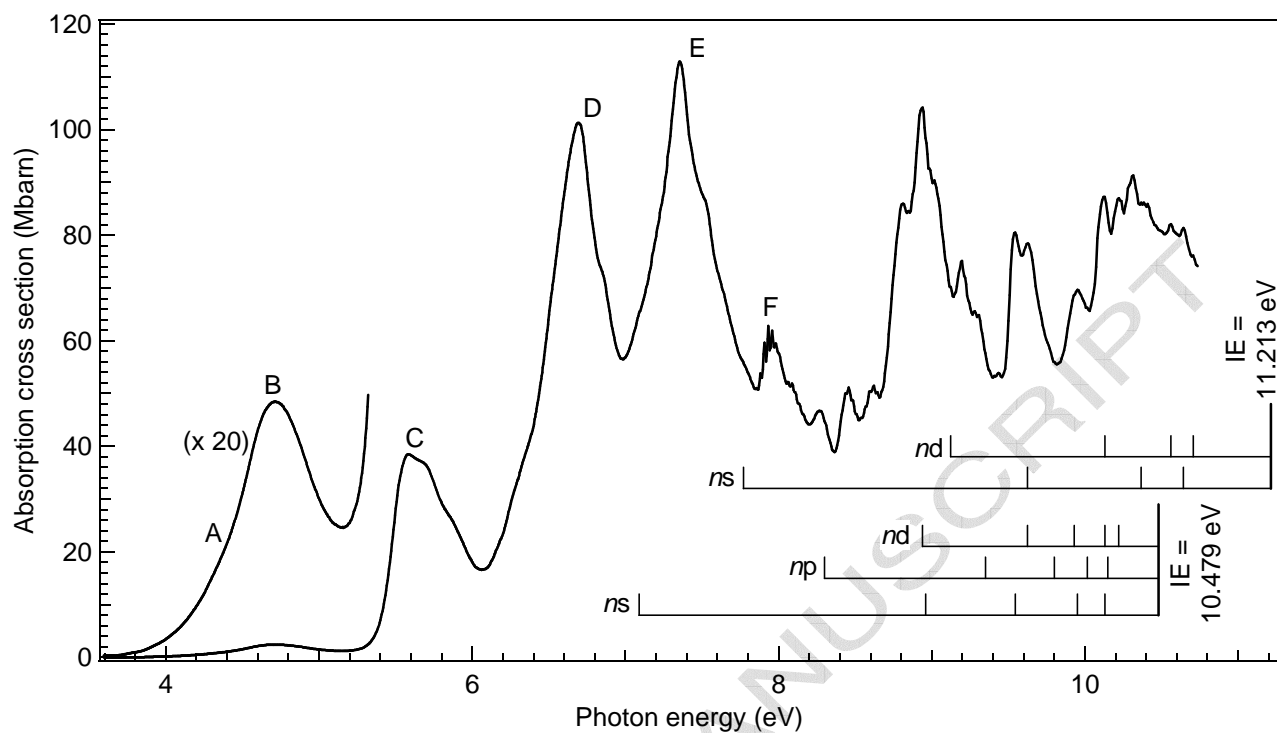


Figure 2: The absolute absorption cross section of iodopentafluorobenzene in the Rydberg state region

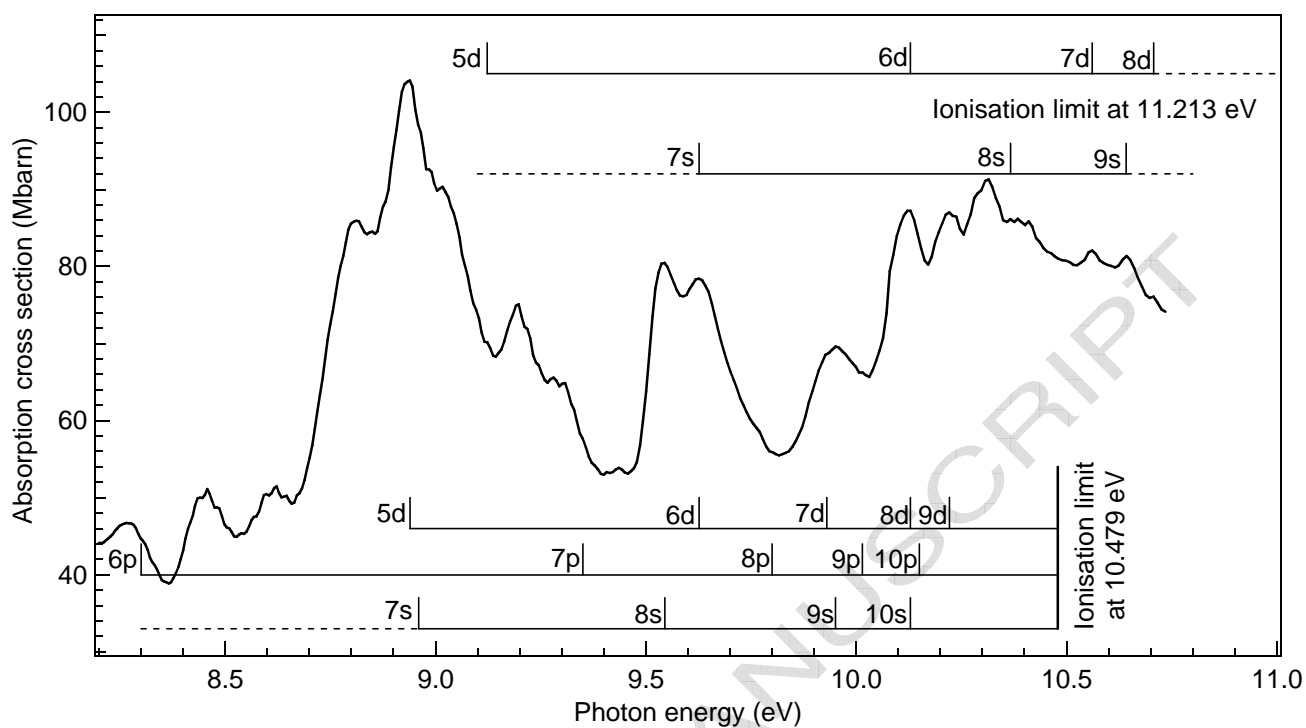


Figure 3: Compiled He(I) photoelectron spectrum of iodopentafluorobenzene in the 9.0 - 16.6 eV region. (* $N_2^+ X \ ^2\Sigma_g^+$, $v' = 0$ produced by the He β line ; ** $N_2^+ X \ ^2\Sigma_g^+$, $v' = 0$ produced by the He β line ; *** $N_2^+ X \ ^2\Sigma_g^+$, $v' = 1$ produced by the He α line).

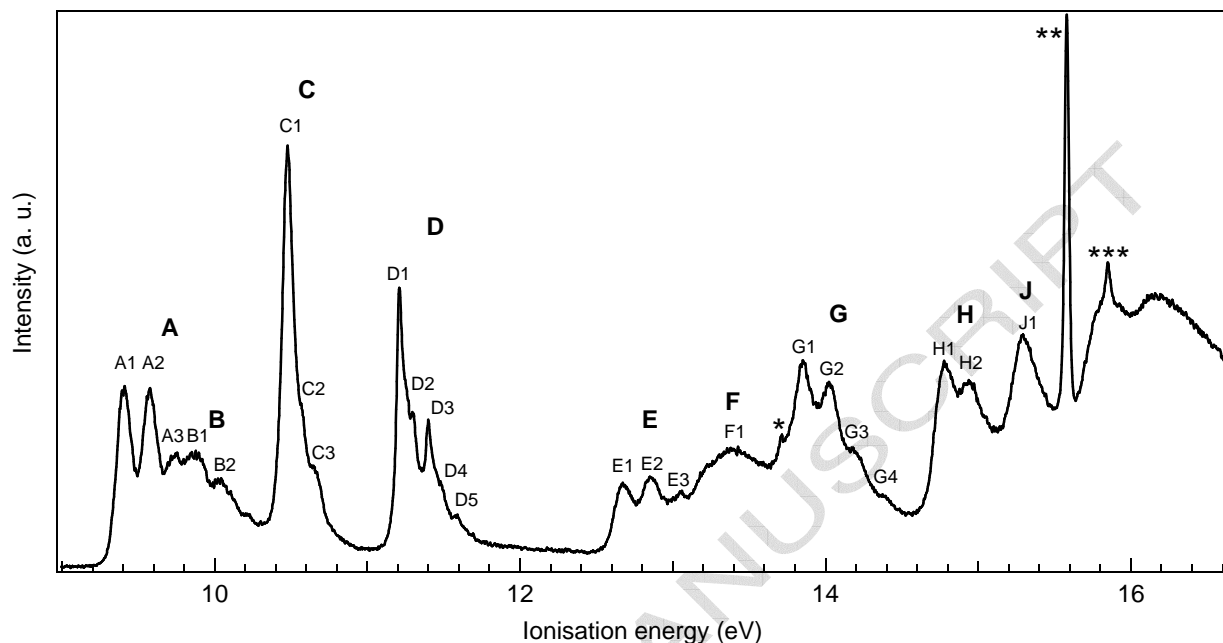


Figure 4: Deconvoluted He(I) photoelectron spectrum of iodopentafluorobenzene in the 9.0 – 10.9 eV region. See text for the attribution of the vibrational features.

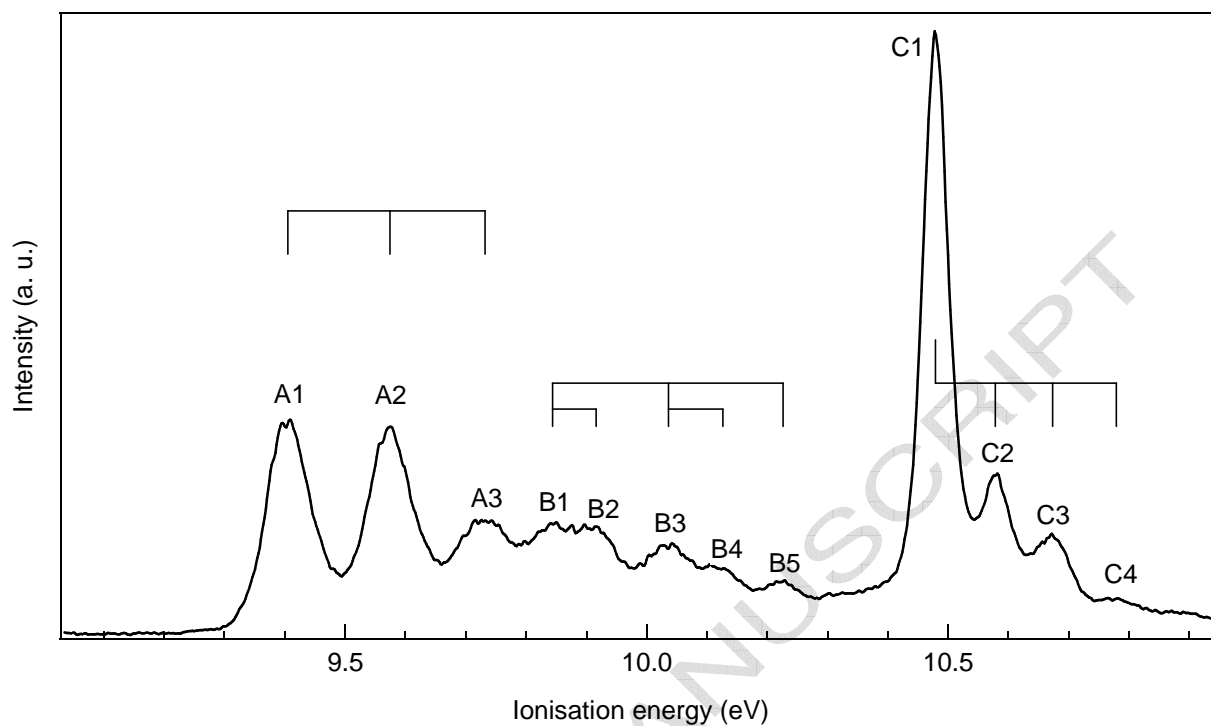


Figure 5: Total photolysis and local lifetime of iodopentafluorobenzene in the terrestrial atmosphere at altitudes between 0 and 50 km. The dotted lines are provided as a guide for the eyes.

